Studies of magnetic and structural properties of Ni-Mn-Ga Heusler-type microwires

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We report on fabrication, magnetic and structural properties of Heusler-type glass coated Ni_2MnGa microwires (metallic nucleus diameter of 44 μm, total sample diameter 82 μm) prepared the modified Taylor-Ulitovsky method. After annealing above 500 $^\circ$C microwires showed ferromagnetic behaviour with well defined easy axis along the wire's axis and Curie temperature around 315 K. X-ray diffraction of annealed at 550°C microwire allowed to determine that microwires have tetragonal martensitic structure with a lattice parameters a = 3.75 Å and c = 6.78Å. The maximum entropy change at magnetic transition was -0.7 $Jkg^{-1}K^{-1}$.

1. Introduction

Magnetic shape-memory alloys (MSMAs) attract considerable attention within last few years owing to significant magnetic-field-induced strain (MFIS), also referred as the "magnetic shape-memory effect" originated from coupling between magnetic and structural ordering. Such strain is produced by the field-induced rearrangement of martensitic variants observed in the low-temperature phase and originated from the magnetic-field-induced motion of twin boundaries [1-4]. Consequently, the magnetic shape-memory effect is useful for actuation purposes and the inverse effect may be utilized for sensing and energy harvesting applications [5]. Additionally, the direct and inverse magnetic shape-memory effects cause magnetic field-induced superelasticity, which is the magnetically-induced recovery of a large mechanically-induced deformation [6].

It is worth mentioning, that MFIS effect originated by magnetic-field-induced motion of twin boundaries has been earlier observed in some ferroelectrics at the beginning of 90-th [7].

The MSMAs usually exhibit a thermoelastic martensite transformation and may change their shape between two states continuously upon heating and cooling [1,2,8]. Consequently martensitic transformation of MSMAs may be induced by stress or magnetic field. The coupling between magnetic and structural ordering in conjunction with the magnetic and structural transformations gives rise to a number of interesting phenomena, such as the magnetic-field-induced martensitic transformation and its reverse transformation, [8] giant magnetoresistance [9], electric polarization [7,10] and the magnetocaloric effect, [11,12].

One of the alloys, where large MFIS values (till 10%) have been achieved, is Ni-Mn-Ga single crystals. In fact MFIS depends on crystalline structure (grain size, size distribution) [13,14]. For example, polycrystalline Ni-Mn-Ga with small grains shows quite small MFIS (< 0.01%), because grain boundaries effectively suppress the twin boundaries motion [6]. But higher MFIS (2–9%) can be achieved in polycrystalline samples with reduced incompatibilities between grains [15].

As mentioned above, some of Heusler-type materials exhibit large magnetocaloric effect, MCE, i.e., the ability to absorb or produce heat as the result of the application of external magnetic fields, H. Since the MCE originates from change of the magnetization induced by magnetic field, and characterized by a change in magnetic entropy, magnetic systems that undergo field induced phase transitions, characterized by large, sharp changes in magnetization near or above room temperature, are of considerable interest as promising MCE materials. One such system is the Ni-Mn-Ga Heusler alloys [11,12].

It is worth mentioning, that from the point of view of technological applications, miniaturizing of MSMA-based devices based on small-size MSMA particles, wires, ribbons, films, bi- and multilayers, pillars is quite important [6]. The main problem with Ni-Mn-Ga alloys is that they are quite brittle [6].

Regarding modern magnetic materials with reduced dimensionality, thin glass-coated magnetic microwires (typical metallic core diameters, d, between 1 and 30 μm and the thickness of the insulating glass coating between 0,5 and 20 μm) produced by Taylor- Ulitovsky technique attracted growing attention within the last years [16,17]. One of the advantages of this fabrication technique is that it allows the fabrication of few km long glass-coated

metallic microwires. This method allows fabrication of such composite microwires with amorphous, nanocrystalline, microcrystalline or granular structure [17-20]. Recently amorphous microwires already found industrial application for magnetic field detection [21]. Both amorphous and nanocrystalline microwires are quite promising from the point of view of technological applications owing to unusual magnetic properties such as the giant magnetoimpedance (GMI) and the magnetic bistability (MB) effects [17-19].

Recently, successful preparation of microwires with giant magnetioresistance , GMR, effect related with its granular structure [18, 22], microwires exhibiting mixed amorphous-crystalline structure [23], with magnetocaloric effect [18, 24], shape memory effect [25] and from Heusler alloys [17, 26, 27] have been also reported.

One of the advantages of the Taylor- Ulitovsky technique allowing fabrication of microwires is related with the composite character of such microwires. Therefore, fabrication of relatively long pieces of glass-coated microwire even of brittle alloys, which is the case of brittle Ni-Mn-Ga alloy, might be possible [6].

Consequently in this paper we report on fabrication and characterization of Heusler-type Ni_2MnGa glass-coated microwires using Taylor-Ulitovsky method. We report results on magnetic and structural properties of Ni_2MnGa glass coated microwires with metallic nucleus diameter of 44 μm.

2. Experimental

Ni_2MnGa ingot has been prepared using arc-melting of pure elements. Taylor-Ulitovsky technique has been employed for fabrication of few meters long Ni_2MnGa glass-coated microwires (metallic nucleus diameter, d about 44 μm, total microwire diameter about 80 μm), as described elsewhere [17-20]. As-prepared Ni2MnGa microwire has been annealed at 823 K for 5 minutes in the Helium protective atmosphere.

Samples structure and phase composition we studied using High-energy X-ray powder diffraction measurements, performed at HASYLAB at DESY (Hamburg, Germany) at the BW5 experimental station located the DORIS III positron storage ring operating at electron energy of 4.45 GeV and a stored current in the range of 140–100 mA. All measurements were performed at room temperature in transmission mode. The samples were illuminated for 60 s by a well collimated 1 mm^2 incident beam of photon energy 100,577 keV (λ = 0.12327 A°). XRD patterns were stored by a 2D detector (mar345 image plate). The background intensity was subtracted directly from the 2D XRD pattern and the result was integrated to 2θ-space by using the program Fit2D [12].

We measured magnetization curves at temperatures between 10 and 400K using SQUID Quantum Design MPMS XL. Before recording the virgin magnetic curve, the sample was cooled down to 250 K at zero field and then heated up to the measuring temperature to maintain the same thermomagnetic history.

3. Results and discussion

As-prepared microwires did not show ferromagnetic ordering. Annealing at 823 K (annealing time 5 min) results in drastic change of magnetic properties: annealed sample below approximately 320 K show magnetization curves typical for ferromagnetic materials (Fig.1). Magnetization versus temperature dependence exhibits typical for ferromagnetic materials behaviour with Curie temperature about 315 K (Fig. 2).
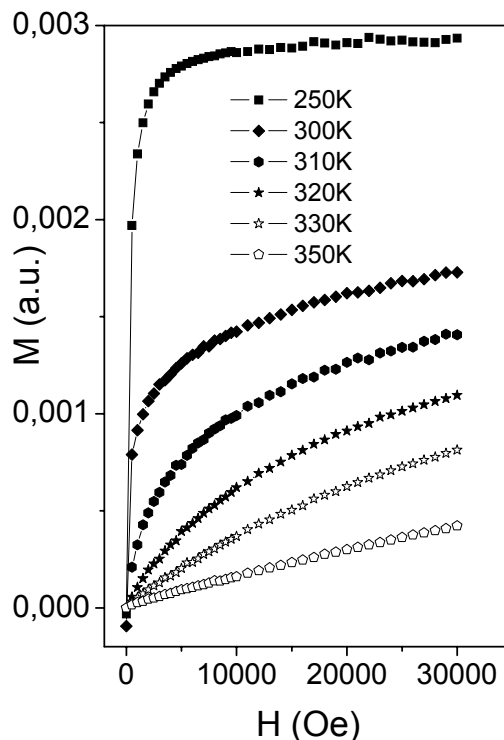

Fig. 1. Magnetization curves of Ni_2MnGa microwires annealed at 823 K measured at different temperatures
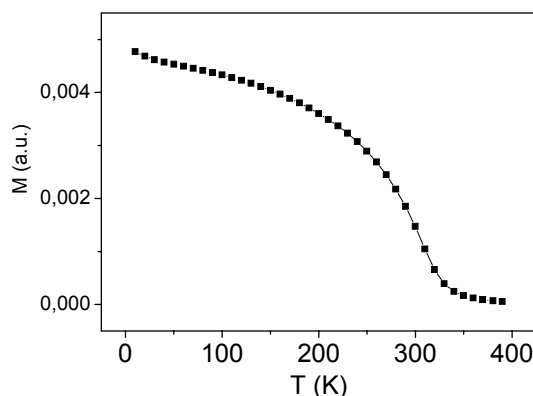

Fig.2. Temperature dependence of magnetization for Ni_2MnGa microwires annealed at 823 K

Consuiderable influence of thermal treatment on magnetic character of produced microwire should be

explained considering strong internal stresses induced during the simultaneous rapid solidification of the metallic nucleus inside the glass coating [17-20]. As shown elsewhere, strength of induced internal stresses is determined by the ρ–ratio between the metallic nucleus diameter, d, and total composite wore diameter, D, being induced by the difference in the thermal expansion of the metallic core and glass coating. Strength of internal stresses increases with decreasing the ρ– ratio [28]. Additionally these internal stresses have tensor character, being mostly of axial character [28]. Consequently, considering important role of stresses on martensitic transformation of MSMAs[5] we can expect some changes in structural and magnetic properties of microwires as-compared with other MSMAs.

We also measured hysteresis loop in axial and perpendicular with respect to the wire´s axis directions. Axial hysteresis loop Ni_2MnGa microwire exhibits an increase of the magnetization till3 kOe with coercivity of about 100 Oe(fig.3). The decrease of magnetization at higher fields should be attributed to the diamagnetic contribution from the glass-coating (Fig. 3).
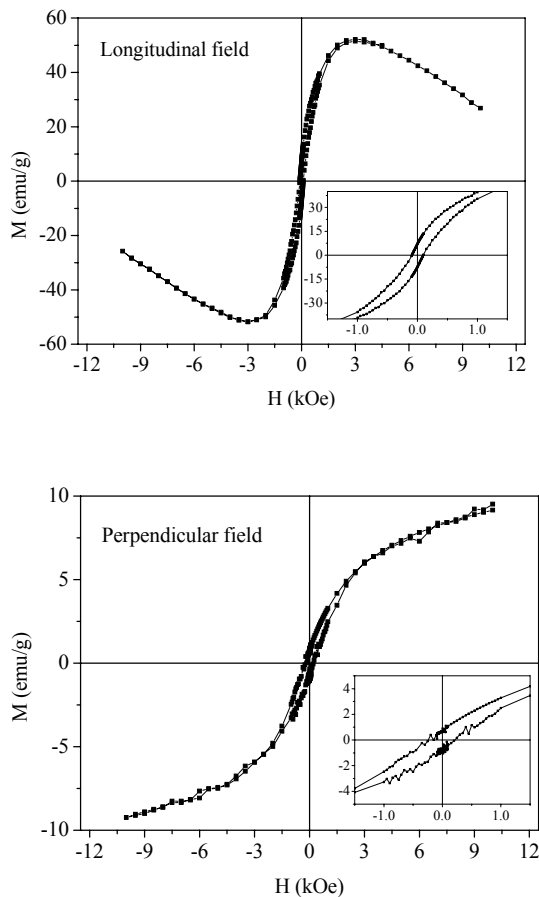
On the other hand, gradual increase of magnetization within the whole applied field region (up to 10 kOe) has been observed when the field is applied to the perpendicular direction to the wire's axis (Fig. 3). In this case the coercivity about 200 Oe has been observed.

From comparison of the hysteresis loops measured in both directions, the longitudinal easy magnetization axis should be assumed. Observed magnetic anisotropy can be explained considering few mechanisms for such behaviour: the magneto-crystalline anisotropy related either with a structural texture and the presence of the tetragonal structure or the shape anisotropy, typical for thin wires. Additionally strong axial stresses related with composite character of cast microwires should be considered.

From magnetization curves, measured at different temperatures, T, we obtained the entropy change, ΔS, as described elsewhere [29] (Fig. 4). ΔS(T) exhibits peak with broad maximum at about 315 K. The peak position at 315 K correlates well with the Curie temperature, estimated from dependence of magnetization on temperature (Fig.2). Observed entropy change of about 0.7 $J.kg^{-1}K^{-1}$ is similar to early observed in ribbons with similar composition exhibiting magnetic transition [30].
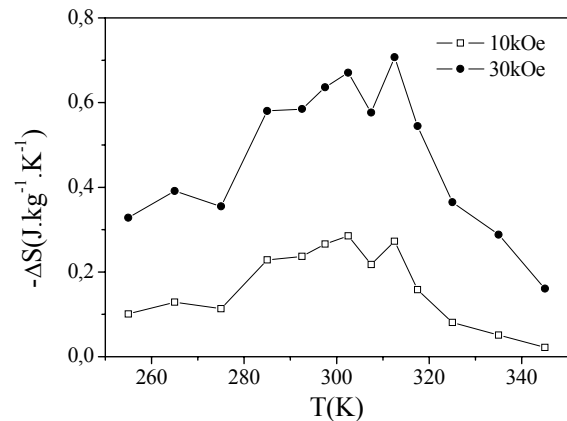

Fig.4. The entropy change of Ni_2MnGa microwires annealed at 823 K, determined from M(H) measured at different temperatures.

Fig. 3. Hysteresis loops for Ni_2MnGa microwires annealed at 823 K measured in longitudinal (left) and perpendicular (right) direction of applied field measured at room temperature. Inset shows zoom to the central part of the loops.

Observed temperature dependence of magnetization should be attributed to the structural and magnetic transformations. It is worth mentioning, that the saturation magnetization of austenite is smaller [31] and Curie temperature of austenitic and martensitic phases are different. A gradual structural change is expected in such materials [32,33]. Consequently, observed temperature dependence of magnetic properties should be interpreted considering both changes of magnetization in each phase and a structural change upon heating. Therefore, sharp magnetization change in vicinity of both structural and magnetic transformation can be the reason of observed MCE effect.

From the X-ray diffraction of annealed microwires (see X-ray spectra on Fig. 5) we identified, that the crystalline structure presents single phase with tetragonal martensitic structure (lattice parameters a = 3.75 Å and c = 6.78Å). As-compared with bulk materials, observed structure presents elongated c axis [34, 35]. Regarding lattice deformation along the C-axis, we suppose, that strong stress induced during fabrication process by the difference between thermal expansion coefficients of metallic nucleus surrounded by the glass-coating must be the reason of such lattice parameters changes.
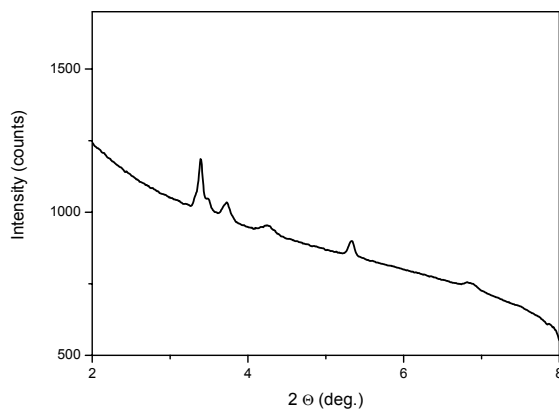

Fig.5. X-ray spectra of Ni$_2$MnGa microwire annealed at 823 K measured at room temperature.

It is worth mentioning, that the XRD pattern taken at just room temperature is not conclusive in respect to the overall behaviour of the sample. Observed magnetic transition temperature, 315 K might not represent the Curie temperature for the martensite but also the austenite finish temperature, in case that the austenite-like phase might have a transition temperature lower than 315 K. To clarify these points additional measurements are needed.

It is worth mentioning, that utilization of Taylor-Ulitovsky technique for fabrication of glass-coating microwires allows fabrication of long peaces of Heusler-type Ni$_2$MnGa microwires and also resulted in improvement of mechanical properties of such composite Ni$_2$MnGa microwires. This might be important from the point of view of future technological applications. Previously it was well established, that unlike ductile alloys, brittle Ni-Mn-Ga cannot be cold-drawn to create fibers [5]. At the same time, strong internal stresses induced during fabrication process by the difference between thermal expansion coefficients of metallic nucleus surrounded by the glass-coating did not allowed achievement of ferromagnetic ordering in as-prepared state and additional heat treatment is needed to relax internal stresses.

4. Conclusions

Consequently, we report on fabrication and characterization of a Heusler-type glass coated Ni$_2$MnGa microwires with metallic nucleus diameter of 44 μm using Taylor-Ulitovsky method. We performed first magnetic and structural characterization of annealed samples exhibited ferromagnetic behaviour with Curie temperature about 315 K. Heat treated Ni$_2$MnGa microwires exhibited well defined easy axis parallel to the wire's axis and tetragonal martensitic structure with a lattice parameters a = 3.75 Å and c = 6.78Å. We found also the magnetocaloric effect in vicinity to the Curie temperature with the maximum entropy change of -0.7 Jkg^{-1}K.$^{-1}$.

Utilization of the Taylor-Ulitovsky method for fabrication of composite metallic microwire coated by glass allowed improvement of mechanical properties of such composite Ni$_2$MnGa microwires and fabrication long (few meters) Heusler-type Ni$_2$MnGa glass-coated microwires. On the other hand strong internal stresses arising from the difference in thermal expansion of the metallic core and glass coating require additional heat treatment for relaxation of such internal stresses to achieve the ferromagnetic ordering with Curie temperature about room temperature.

Acknowledgements

References

[1] K. Ullakko , J. K. Huang , C. Kantner, R. C. O'Handley, V.V. Kokorin , Applied Phys. Lett., **69**, 1966 (1996).
[2] J. Ma, I. Karaman , Science, **327**, 1468 (2010).
[3] P. Müllner , G. Kostorz , Mater. Sci. Forum **583**, 43 (2008).
[4] R. Tickle, R.D. James, J. Magn. Magn. Mater. **195**, 627 (1999)
[5] A. Nespoli, S. Besseghini, S. Pittaccio, E. Villa, S. Viscuso, Sens. Act. A, **158** , 149 (2010).
[6] D C. Dunand, P. Müllner, Adv. Mater., **23**, 216 (2011).
[7] B. K. Ponomarev, S. A. Ivanov, V. D. Negrii, A. P. Zhukov, B. S. Red`kin, V. N. Kurlov, A. K. Zvezdin, Yu. F. Popov, Ferroelectrics, **151**, 103 (1994).
[8] H. E. Karaca , I. Karaman , B. Basaran , Y. Ren , Y. I. Chumlyakov , H. J. Maier, Adv. Funct. Mater., **19**, 983 (2009).

[9] V. A. Chernenko, M. Ohtsuka , M. Kohl,
V. V. Khovailo , T. Takagi , Smart Mater. Struct.
14, 245 (2005).

[10] A.P. Hammersley, S.O. Svensson, M. Hanfland,
A.N. Fitch, D. Hausermann High Pressure Res.,
14, 235 (1996).

[11] K. Otsuka, C. M. Wayman, Shape Memory
Materials, Cambridge (1998) .

[12] K. A. Gschneidner , V. K. Pecharsky , A. O. Tsokol ,
Reports on Progress in Physics **68**, 1479 (2005).

[13] G. Kostorz , P. Müllner, Z. Metallkunde
96, 703 (2005).

[14] O. Söderberg , I. Aaltio, Y. Ge, O. Heczko,
S. P. Hannula , Mater. Sci. Eng. A, **80**, 481 (2008).

[15] M. Chmielus , X. X. Zhang , C. Witherspoon,
D. C. Dunand , P. Müllner, Nat. Materials
8, 863 (2009).

[16] D.C.Jiles, Acta Materialia, **51**, 5907 (2003).

[17] V. Zhukova, M. Ipatov, A Zhukov, Sensors,
9, 9216 (2009).

[18] A. Zhukov, V. Zhukova, Magnetic properties and
applications of ferromagnetic microwires with
amorphous and nanocrystalline structure, Nova
Science Publishers, Inc. 400 Oser Avenue, Suite
1600 Hauppauge, (2009).

[19] M. Vazquez, H. Chiriac, A. Zhukov, L. Panina,
T. Uchiyama, Phys. Status Solidi A **208**, 493 (2011).

[20] H.Chiriac, T.A.Ovari, Progress in Material Science
40, 333 (1996).

[21] see http://www.aichi-mi.com product AMI-306.

[22] A. Zhukov, J. Gonzalez and V. Zhukova, J. Magn.
Magn., Mater. **294**, 165 (2005)

[23] A. Zhukov, C. Garcia, V. Zhukova, V. Larin,
J. González, J. J. del Val, M. Knobel, J. M. Blanco,
J. Non-Cryst. Sol. **353**, 922 (2007).

[24] M. I. Ilyn, V. Zhukova, J. D. Santos, M. L. Sanchez,
V. M. Prida, B. Hernando, V. Larin, J. Gonzalez,
A. M. Tishin, and A. Zhukov, Phys. Stat. Sol.(a),
205, 1378 (2008).

[25] Y. Chen, X. Zhang, D. C. Dunand, and C. A. Schuh,
Appl. Phys. Lett. **95**, 171906 (2009).

[26] C.M. Craciunescu, A. Ercuta, I. Mitelea, M. Valeanu,
V.S. Teodorescu, N. Lupu, and H. Chiriac, Eur. Phys.
J. Special Topics **158**, 161 (2008)

[27] C. García, V. M. Prida, V. Vega, J. L. Sánchez
Llamazares, J. J. Suñol, Ll. Escoda, M. L. Sánchez,
J. Ribot, and B. Hernando, Phys. Status Solidi A,
206, 644 (2009).

[28] H. Chiriac, T.A. Ovari and A. Zhukov, J. Magn.
Magn. Mater. **469**, 254 (2003).

[29] K. A. Gschneidner, V. K. Pecharsky, J.Appl. Phys.
86, 565 (1999).

[30] B.Hernando, J.LSanchez Liamazares, J.D.Santos,
V.M.Prida, D.Baldomir, D.Sarentes, R.Varga,
J.Gonzales, Appl. Phys. Lett. **92**, 1 (2008).

[31] A. B. Pakhomov, C. Y. Wong, X. X. Zhang,
G. H. Wen, G. H. Wu, IEEE Trans. Magn.
37(4), 2718 (2001).

[32] V. V. Khovaylo, K. P. Skokov, O. Gutfleisch,
H. Miki, T. Takagi, T. Kanomata, V. V. Koledov,
V. G. Shavrov, G. Wang, E. Palacios, J. Bartolomé,
R. Burriel, Phys.Rev B **81**, 214406 (2010)

[33] M.Sofronie, F. Tolea, V. Kuncser, M. Valeanu
J.Appl.Phys. **107**, 113905 (2010).

[34] D. Y. Cong, Y. D. Zhang, Y. D. Wang, M. Humbert,
X. Zhao, T. Watanabe, L. Zuo, C.Esling, Acta
Materiala, **55**, 4731 (2007).

[35] Y.D.Wang, D.Y.Cong, R.Lin Peng, P. Zetterstrom,
Z.F.Zhang, X.Zhao, L.Zuo, J.Mater.Res.
21(3) 691 (2006).

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